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Commentary Experiments on the Formation of Fe_3O_4 Precipitate from Aqueous Solution.

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Three different experiments have been made in simplified reaction conditions in order to elucidate the processes of formation of Fe_3O_4 precipitate. Starting iron salts, ferrous and ferric sulphates, were reacted at room temperature. It has been shown that (i) depending upon the pH value of the solution under reaction, Fe_3O_4 is formed directly by neutralization reaction or indirectly by way of the intermediate precipitates and (ii) the intermediate precipitates do not react in the solid state but dissolve very slowly into the solution and Fe_3O_4 precipitate is formed by the reaction between ferrous and ferric hydroxo complexes in the solution.

INTRODUCTION

It is well known that Fe_3O_4 can be prepared from aqueous solutions by precipitation methods. These methods can be roughly classified into the following three reaction systems. (1) Co-precipitation system; adding an alkaline solution to a mixed solution of ferrous and ferric salts,[1~3] (2) Hydrothermal system; heating an aqueous solution of ferrous hydroxide,[4~5] (3) Oxidizing system; oxidizing an aqueous solution of ferrous precipitates such as basic sulphate, carbonate and hydroxide, by air or oxidizing reagents.[1,6,7]

The processes of Fe_3O_4 formation in these reaction systems are different from each other. On the mechanism of Fe_3O_4 formation, for example, several workers suggested that Fe_3O_4 particle was formed by surface oxidizing or solid-solid reaction of intermediate precipitates in the solution. But this suggestion can not affirmed since the present author has been found that the shape and volume of the Fe_3O_4 particle formed in the solution do not resemble those of the intermediate precipitates. In order to clarify the mechanism of Fe_3O_4 formation which can explain the processes of the above reaction systems, still more detailed experiments are needed.

The author's group has studied these problems since fifteen years ago and made clear the processes of Fe_3O_4 formation in the various reaction systems. In this paper, the results of some preliminary experiments on the co-precipitation system are reported. The results on the other reaction systems will be published separately.

MATERIALS AND pH MEASUREMENT

Chemical reagents of analytical grade were used in the experiment. The water free from oxygen used was made by bubbling nitrogen gas into the distilled water kept in the boiling state.

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The measurement of pH value was made by a Horiba glass electrode pH meter.

EXPERIMENTAL

I. Titration experiment of the solution containing ferrous and ferric ions.

In order to infer the relation between the pH value of the solution containing ferrous and ferric ions after homogenization and the kind of the precipitates formed, the titration experiment was conducted as follows.

300 ml of the solution containing 0.333 *M*-ferrous sulphate, 0.333 *M*-ferric sulphate (the concents of ferrous and ferric ions in the solution are in the atomic ratio of 1 to 2) and 0.0016 *M*-sulfuric acid was titrated very slowly with 2.0 *N*-sodium hydroxide solution in the atmosphere of nitrogen.

At the beginning of titration a black precipitate, possibly, Fe_3O_4 was formed at the location where the alkaline solution met the iron salt solution because of high pH value there. Then the homogenization of the solution went on by stirring, the pH value was allowed to reach an apparent equilibrium and the precipitate of Fe_3O_4 formed became unstable and was substituted by another one. As the titration went on further, the pH value increased and, consequently, some other precipitate was formed at some locations of the solution every moment when the alkaline solution for titration was added. This precipitate sometimes disappeared and another precipitate

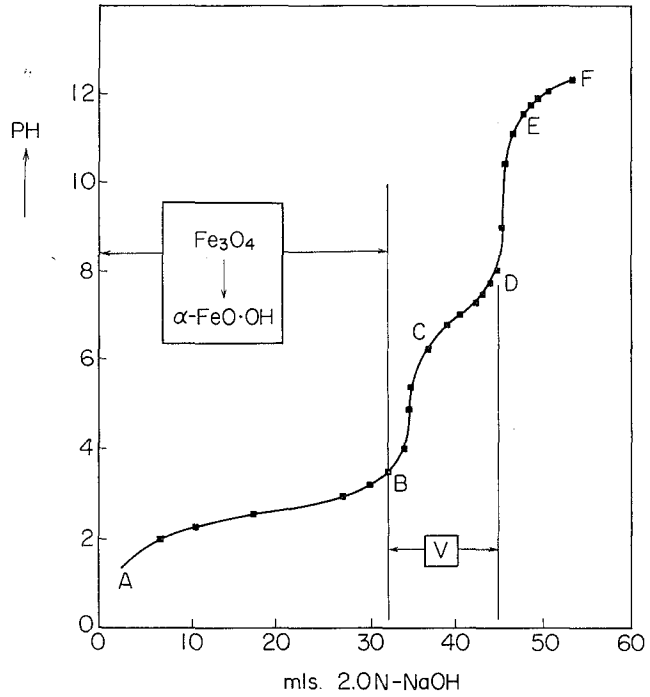

Fig. 1. Experimental titration curve of the solution containing ferrous and ferric sulphates ($Fe^{2+}/Fe^{3+}=0.5$) with 2.0 *N*-NaOH solution at room temperature; $V=Fe(OH)_2+FeOOH \rightarrow$ green rust $II+Fe_3O_4$.

was formed. Figure 1 shows the relation between the pH value after homogenization and the quantity of 2 *N*-NaOH solution added for the titration. The curve drawn in the figure has two steeps BC and DE showing the rapid elevation and three steps AB, CD and EF showing gradual elevation. The nature of the curve may be explained as follows by taking the author's observation into account.

Up to the point B from the point A, the locally formed black precipitate which was found to be ferromagnetic and possibly Fe_3O_4 disappeared or converted into the brownish and non-ferromagnetic precipitate as the pH value dropped to the value shown in the figure by the homogenization. Since the superfine particles of Fe_3O_4 are very unstable in the solution whose pH value is less than about 4, the Fe_3O_4 precipitate formed redissolves into the solution and forms ferrous ions and ferric hydroxo complex ions. Of these two kinds of ions the former will remain as such while the latter is destined to form the precipitate of α-FeOOH. In other words, up to the point B in the curve all of the ferrous salt dissolved coexists with the ferric precipitate and at the point B no ferric ion dissolved is present. As the titration proceeded beyond B, the pH value suddenly increased and after the elevation of the pH value to the point C, the value elevated slowly as the quantity of alkali added. This means that different ferrous precipitates are formed in the solution. In the range from the point C to D, a white precipitate, possibly, $Fe(OH)_2$ was formed and coexisted with that of α-FeOOH already present. After a few minutes, a new green precipitate was formed in the solution.

It has been known from our experimental results that Fe_3O_4 is directly formed from an aqueous sulphate solution of $Fe(OH)_2$ by oxidation reaction when the pH value of the solution is above 9 while Fe_3O_4 is formed in the solution containing $Fe(OH)_2$ and the green precipitate, called green rust II, in the pH range of 6.5 to 9. The green precipitate formed in the sulphate solution, has a hexagonal crystal structure (a_o=3.174 Å, c_o=10.94 Å)[7] and contains about 60% ferrous ion to the total iron ions. Accordingly, this green precipitate is roughly represented by the formula $Fe(OH)\ OFe(OH)_2$ and, in the co-precipitation system, is thought to change into Fe_3O_4 by reacting with α-FeOOH which remained in the solution. On the other hand, the particles of Fe_3O_4 formed in the various reaction systems are cubic in the shape. The intermediate precipitates are not cubic, but hexagonal or needle like. From the facts described above, the formation of Fe_3O_4 may be attributed to the presence and reaction of ferrous and ferric hydroxo complexes in the solution. The hydroxo complexes are supplied by, respectively, $Fe(OH)_2$, $Fe(OH)OFe(OH)_2$ and α-FeOOH.

Thus the gradually elevated part from the point C to the point D in the curve corresponds to the reaction by the following equations besides the formation of $Fe(OH)_2$ and indicates that the rate of each reaction is very slow at room temperature. Each precipitate may be formed by reaction as follows.

$$Fe(OH)_2+x.H_2O=[Fe^{2+}(OH)_{2-x}]^*+x.OH^- \quad (pH>7) \tag{1}$$

$$FeOOH+y.H_2O=[Fe^{3+}(OH)_{3-y}]^*+y.OH^- \quad (pH<3) \tag{2}$$

$$[Fe^{2+}(OH)_{2-x}]+[Fe^{3+}(OH)_{3-y}]+(x+y).OH^-\rightarrow Fe(OH)OFe(OH)_2 \quad (4<pH<6.5) \tag{3}$$

* $[Fe^{2+}(OH)_{2-x}]$ and * $[Fe^{3+}(OH)_{3-y}]$ refer to ferrous and ferric hydroxo complexes, respectively.

$$[Fe^{2+}(OH)_{2-x}]+2[Fe^{3+}(OH)_{3-y}]+(x+2y).OH^- \rightarrow Fe_3O_4 \quad (pH > 6.5) \qquad (4)$$

as apparent net reaction,

$$Fe(OH)_2+FeOOH \rightarrow Fe(OH)OFe(OH)_2 \qquad (5)$$

$$Fe(OH)OFe(OH)_2+FeOOH \rightarrow Fe_3O_4 \qquad (6)$$

$$Fe(OH)_2+2FeOOH \rightarrow Fe_3O_4 \qquad (7)$$

The sudden rise of the curve from the point D to the point E means that almost all of the ferrous ions are precipitated.

II. Neutralization experiment in which two kinds of solution containing NaOH, and ferrous and ferric ions are calmly brought into contact in a glass tube, horizontally set and provided with a three way cock.

In the preceding experiment, the first precipitate formed at the moment of addition of the titration solution disappeared as the homogenization of whole the solution proceeded as in ordinary case of the titration and so the precise observation of the precipitate was hardly possible. In the present experiment, care has been taken to let the precipitation reaction proceed very calmly by avoiding mechanical disturbance as possible as it could be, so as to make the precise observation about the precipitates.

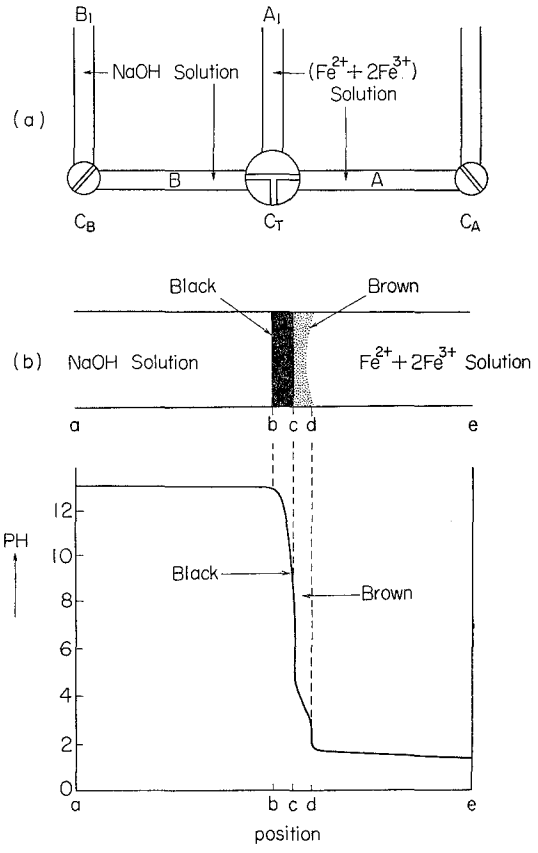

Fig. 2. Schematic illustration of apparatus (a). Colors of precipitates formed and pH value of each position in the passage of cock C_T (b).

The apparatus used in the present experiment is shown schematically in Fig. 2–(a). The main glass tube provided with three cocks has two side tubes A_1 and B_1. The part A was filled with the iron salt solution containing ferrous and ferric sulphates (the ratio of ferrous to ferric ions is 1 to 2 in the atomic ratio) by passing the solution from the side tube A_1 through the cock C_T and the part B was filled with the solution of sodium hydroxide by passing it from the side tube B_1 through the cock C_B. After keeping the main glass tube in the horizontal position, the three way cock C_T was turned cautiously to let the solution in A and B come into contact with each other and the solution contained in the passage of the cock C_T was observed with a magnifying glass. The passage prepared in the cock C_T was somewhat wider than those used in conventional experiments.

In the contact layer of two kinds of the solution in the above passage, a thin black layer, possibly, of Fe_3O_4, was observed and after a few minutes, adjacent to this layer a brownish layer, possibly, of α-FeOOH or γ-Fe_2O_3 was observed to be formed. The supposed figures shown in Fig. 2–(b) show the thickness of each layer and the pH value along the passage of the cock involving the two colored layers, respectively. It was also observed that as the reaction went on further, the black layer as well as the brownish layer became wider. Neither white nor colored precipitate was formed, however, in the part B.

From the result of this experiment, it is concluded that Fe_3O_4 precipitate can be formed directly from the solution when the iron salt solution meets with alkaline solution.

III. Experiment in which two kinds of the sedimented layer containing, respectively, $Fe(OH)_2$ and α-FeOOH are calmly brought into contact.

A certain quantity of ferrous sulphate solution was poured into the concentrated sodium hydroxide solution contained in a glass bottle shown in Fig. 3–(a) so as to precipitate all of the ferrous ion by adjusting the pH value of the resulting solution to

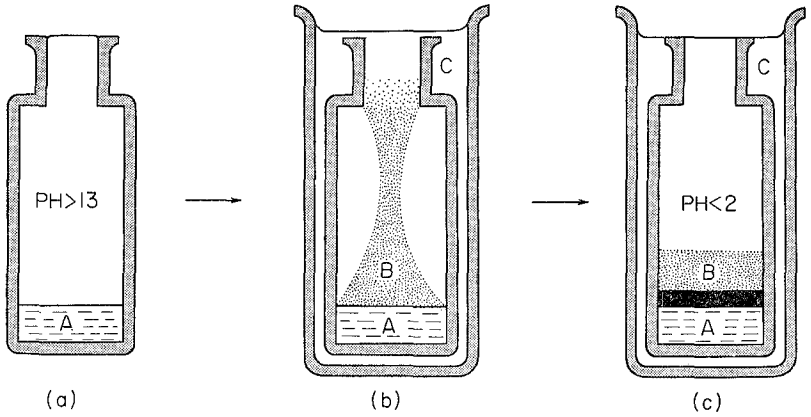

Fig. 3. Schematic illustration of the formation of Fe_3O_4 (black precipitates) between $Fe(OH)_2$ and α-FeOOH ; A = $Fe(OH)_2$, B = α-FeOOH, C=Fe^{3+}ion.

above 13. After all of the white precipitate, $Fe(OH_2)$, sedimented as shown in the same figure, a distinct white layer of sedimentation was observed.

Then this bottle was settled into the glass beaker, as shown in Fig. 3–(b). The solution of ferric sulphate was poured slowly into the beaker untill the surface of the ferric sulphate solution reached the top of inner bottle. After a few minutes a faintly brownish cloud was observed to be formed over the white layer of $Fe(OH)_2$ in the inner bottle. Then the brownish cloud, possibly, α-FeOOH sedimented gradually, forming a brownish layer upon the white layer. After 50 hours, a black layer was observed to be formed at the boundary part between the two kinds of the sedimented layer as shown in Fig. 3–(c).

In the above experiment, the mutual solid state reaction between the precipitates of $Fe(OH)_2$ and α-FeOOH is not probable. Accordingly, the formation of Fe_3O_4 may be attributed to the reaction as shown in the eq. 1, 2 and 4

COMMENTARY NOTE AND SUMMARY

In the three different experiments, Fe_3O_4 was found to be precipitated in different processes. As the present experiments were made at room temperature, the formation of Fe_3O_4 by the solid state reaction between (i) $Fe(OH)_2$ and α-FeOOH or (ii) α-FeOOH and the green precipitate, $Fe(OH)OFe(OH)_2$, is out of the question. Therefore, the above precipitates are thought to redissolve very slowly in the solution and the Fe_3O_4 precipitate is formed by reaction between ferrous and ferric hydroxo complexes.

The results obtained in the present series of experiments may be summarized as follows.

When the solution containing ferrous and ferric ions is neutralized with alkaline solution gradually, the pH value of the solution elevates not monotonously but alternately with gradual and sudden changes and existing phase or phases correspond to the pH value.

The Fe_3O_4 precipitate is formed directly from the iron salt solution containing ferrous and ferric ions by neutralization or indirectly from the solution containing $Fe(OH)_2$ or the green precipitate and α-FeOOH.

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